



Synthesis and Characterizations of Silver Colloid Nanoparticles Stabilized by Dextran

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Abstract

This study aims to investigate the influence of different concentration of silver nanoparticles in Dextran (Dx) suspension. The silver nanoparticles (AgNPs) were prepared by chemical reduction method using reduction agents, Dextran (Dx) under moderate temperature at different concentration. Three different sample solutions were prepared viz., 0.4, 0.8 and 1.2% (w/v) Dx at a constant temperature (80 °C). Silver nitrate (AgNO₃) was taken as the metal precursor while Dx was used as the solid support and polymeric stabilizer. The formation of nano silver was identified by the color change from white precipitate to yellowish-brown color. Formation of Ag-NPs was determined by UV-Vis spectroscopy where surface plasmon absorption maxima can be observed at 412–437 nm from the UV-Vis spectrum. The synthesized nanoparticles were also characterized by X-ray diffraction (XRD). The peaks in the XRD pattern confirmed that the AgNPs possessed a face-centered cubic and peaks of contaminated crystalline phases were unable to be located. The Fourier transform infrared (FT-IR) spectrum suggested the complexation present between Dx and AgNPs. Scanning Electron Microscopy (SEM) with EDX and Atomic Force Microscopy (AFM) was applied to characterize the morphology, particle size distribution of the AgNPs. The average particle size of the stabilized samples ranged from 10-40 nm. It was demonstrated that this convenient method is versatile to produce silver nanoparticles with controlled size and shape.

Keywords: Colloidal silver nanoparticles; Dextran; Chemical reduction method.

1. INTRODUCTION

Colloidal silver nanoparticle dispersions can be utilized in many applications such as, medicine (antibiotic materials), biochemistry (biosensors), electrochemistry (electrode materials), and optics (color filters). In addition, nanoscale silver particles have found applications in memory devices, cosmetics, and dental restorative materials. However, large-scale production methods for silver particles and nano-particles are frequently based on aqueous processes (Pillai *et al.* 2004). These processes generate particles with hydrophilic surfaces that are difficult to disperse uniformly in organic media. Nanoparticles also have very large surface areas and hence, very high surface energies that drive spontaneous room temperature agglomeration and sintering via secondary recrystallization onto larger particles (Guenther *et al.* 1992; Li *et al.* 2002). In order to overcome these problems, the surface of silver

nanoparticles must be modified in order to make them more hydrophobic and to prevent agglomeration. The surface properties of such modified nanoparticles can be tailored to achieve a desired property by using different functional groups. These surface modified nanoparticles structures offer a number of applications such as conductive materials in gas sensors, reagents for DNA analysis, catalysts, etc. (Brust *et al.* 2002). Such modifications can also improve the stability of the particles and their dispersibility in organic media.

The current investigation supports that use of silver ion or metallic silver as well as silver nanoparticles can be exploited in medicine for burn treatment, dental materials, coating stainless steel materials, textile fabrics, water treatment, sunscreen lotions, etc. And possess low toxicity to human cells, high thermal stability and low volatility. Synthesis of different morphologies of advanced silver nanomaterials (nanotubes, nanowires, nano cubes,

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nanorods, and nanosheets) has been the subject of a large number of researchers in many laboratories (Mulvaney *et al.* 2002; Tan *et al.* 2003; Yu *et al.* 2005; Xie *et al.* 2007). A number of methods were used in the past for the synthesis of silver nanoparticles for example, reduction in solutions (Kim *et al.* 2009), radiation assisted (Henglein *et al.* 2001) chemical and photoreduction in reverse micelles (Esumi *et al.* 1992), thermal decomposition of silver compounds (Zhu *et al.* 2000) and recently via bio- or green-synthesis route (Sharma *et al.* 2009).

A multitude of chemical reduction methods have been applied to synthesize stable and various shapes of silver nanoparticles in water by the use of different reducing agents (ascorbic acid (Al-Thabaiti *et al.* 2008), hydrazine (Khan *et al.* 2009), ammonium formate (Won *et al.* 2010), dimethylformamide (Rodríguez *et al.* 2012) and sodium borohydride. The shape, size and the size distribution strongly depended on the strong and weak tendency of organic substrates to reduce the silver salts. Dextran is a natural macromolecule composed of α -(1-6) linked D-glucose units with varying branches depending on the dextran-producing bacterial strain.

Dextran is a hydrophilic and water-soluble substance, inert in biological systems and which does not affect cell viability. Because of these properties, dextran solutions have been used for many years as blood expanders to maintain or replace blood volume, and studied for uses as a carrier system for a variety of therapeutic agents. Recent studies revealed that the use of dextran as prodrugs component reduces toxicity, offers sustained release and influences the biodistribution properties of various drugs (Kim *et al.* 2001; Bat *et al.* 1996).

In this study, we report the results of the effects of various factors on the formation of AgNPs. Our results indicate that the formation of stable, monodispersed colloidal solutions of silver nanocomposites and silver nanoparticles can be achieved using chemical reduction methods. The materials were prepared in the form of aqueous dispersions using Dx as stabilizing agent, favoring the formation of small metal particles; metal salts as metal precursor and reducing agent. The synthesis was carried out at low temperature ($<80^{\circ}\text{C}$). The properties of nanomaterial were characterized by means of Ultraviolet-Visible (UV-Vis) Spectroscopy, X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM) with EDS and Atomic Force Microscopy (AFM).

2. EXPERIMENTAL METHOD

2.1 Material and Synthesis of Silver NPs

Silver nitrate (AgNO_3 , 99.9%) was purchased from Sd-fine and used as a precursor in the formation of AgNPs. Dx were purchased from Sd-fine and used as both reducing and stabilizing agents. All chemicals were used without further purification. Demonized (DI) water was used as the solvent.

Preparation of Silver NPs was performed by the addition of an aqueous AgNO_3 solution to an aqueous Dx solution. In a typical procedure, 1g of Dx was dissolved in 99g of DI water to prepare a 1wt% solution. The aqueous Dx solution was mixed with 0.05g of AgNO_3 dissolved in 20 ml of DI water in heated at 80°C .

3. RESULTS AND DISCUSSION

3.1. UV-Vis Spectroscopy

The color of the suspension was changing from white to dark violet, when the reaction was carried on. The distinctive colors of colloidal silver appear due to plasmon absorbance. Incident light creates oscillations in conduction electrons on the surface of the nanoparticles and electromagnetic radiation is absorbed (Solmon *et al.* 2007). The color of the solution and the maximum absorbance are related to the size of nanoparticles. This observation has been confirmed by UV-Vis absorbance spectra which are shown in Fig. 1. The absorbance maximum was located at 414, 419 and 421 nm for samples 1 to 3. These data demonstrate that increasing the molar ratio of dextran results in a blue-shift of absorbance spectra. This result indicates that the size of the nanoparticles formed varies with the concentration of dextran, which acts as a reductive agent as well as a stabilizer.

3.2. X-Ray Diffraction (XRD)

Ag nanoparticles synthesized via the chemical reduction method in the AgNO_3 solution with various Dx (0.4, 0.8 and 1.2% (w/v)) concentrations were observed under XRD as shown in Fig. 2a, b and c. The XRD pattern shows two peaks at 38.2° and 44.3° , which are assigned to the (1 1 1) and (2 0 0), planes of face-centered cubic (FCC) Ag (JCPDS File No. 04-0783). The absence of silver oxide peaks indicates that the as-prepared nanoparticles are made of pure silver. The crystal size of the particles calculated from the Scherrer equation, $D = K\lambda/\beta \cos\theta$. Where D is the crystal size of the catalyst, λ the X-ray wavelength (1.5406 \AA), β the full width at half maximum (FWHM) of the catalyst, K is a co-efficient (0.89) and

θ - is the diffraction angle. Whereas the result showed that the crystal size decreasing with increasing the concentration. Where, 4.7nm (a), 4.6nm (b) and 4.4nm (c) for Ag/Dx nanocomposites at constant temperature (80°C). The calculated lattice constant, according to the spacing (dg) of the (1 1 1) plane (Fig2c) and the equation $1/dg^2 = (h^2 + k^2 + l^2)/a^2$ is 0.1807 nm, which is in good agreement with the standard value of 0.1792 nm. Moreover, the sharp and intensive peak at $2\theta = 38.2^\circ$ (111) indicated a highly organized crystal structure of AgNPs.

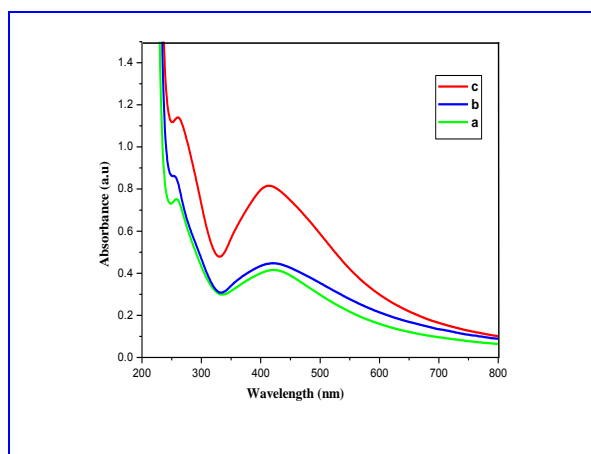


Fig. 1: The UV-visible cures of silver nanoparticles produced under different concentrations of Dx (0.4, 0.8, and 1.2 % w/v) at 80°C

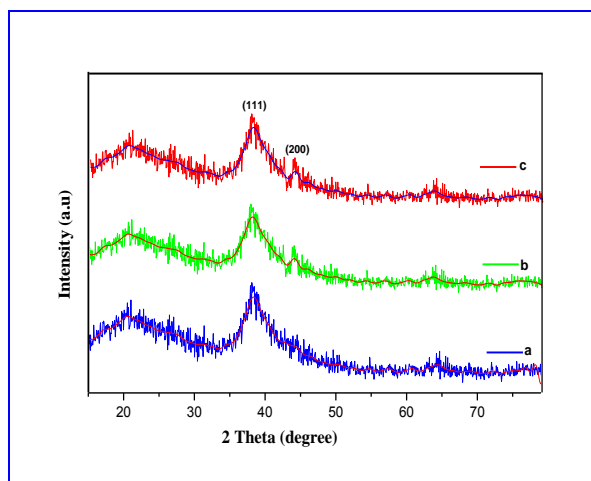


Fig. 2: XRD spectra of Ag/Dx nanoparticles of (a) 0.4, (b) 0.8 and (c) 1.2% w/v at constant temperature(80°C)

3.3. Fourier Transform Infrared Spectroscopy (FT-IR)

Infra-red spectroscopy of the silver capped nanoparticles was also performed (Fig.3a, b and c).

The Fig 3a shows extra peak at 2881cm^{-1} is the CH_2 -stretch, peaks at 1342cm^{-1} , 1279cm^{-1} correspond to C-O vibrations. Hence it is clear that interaction of capping agent with silver nanoparticles causes redistribution of electron density and hence a different set of infra-red active vibration and rotational modes. Ag/Dx showed broad peaks which are shifted towards lower wave numbers with respect to their Fig. (b, c). The band of CO_2 - in the Ag/Dx is shifted to lower wave number as 1653 and 1386cm^{-1} , respectively. The IR peaks at 670 and 840cm^{-1} can be assigned to out of plane vibrations of O-H bond and C-H bond, respectively. The band at 1434cm^{-1} may be due to C-OH deformation vibration with contributions of O-C-O symmetric stretching vibration of carboxyl ate group [34]. The stronger peaks appear in the range of 1150 - 900cm^{-1} mainly attributed to the stretching vibration of C-O-C. An IR peak at $2,924\text{cm}^{-1}$ can be attributed to stretching vibration of CH_2 group. The strong broad peaks at $3,454\text{cm}^{-1}$ corresponds to the OH stretching vibrations of the strong hydrogen bonds from intra and inter-molecular type [35]. It also conform that the synthesized compounds is silver nanoparticles.

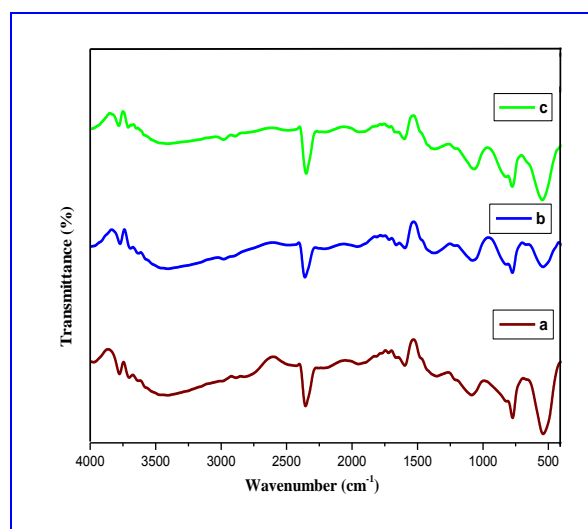


Fig. 3: FT-IR Spectra of (a) 0.4, (b) 0.8 and (c) 1.2% w/v are different concentration of Ag/Dx nanoparticles

3.4 Scanning Electron Microscopy (SEM) with EDS

In Figure 4a, b and 4c are showed SEM micrographs (magnification 5000) was used to investigate the surface morphology of Dextran-Ag nanocomposite three concentrations of 0.4, 0.8 and 1.2% (w/v). SEM images of the samples obtained from the colloidal Ag solutions prepared at 80°C. It confirms the existence of very small and spherical or steroidal nature nanoparticles. Particle size and

distribution from a chemical synthesis are dependent upon the relative rates of nucleation and growth processes, as well as the extent of agglomeration. Despite this, it is difficult to control these rates and, consequently, size distribution. The steroidal nature of the Ag/Dx NPs helps in absorbing the wound exudates and also helps in oxygen exchange to the wound surface. This indicates that silver nanoparticles are formed along with the polymer chains rather than just Ag entrapment in the gel networks. Energy dispersive X-ray analysis (EDS) of silver nanoparticles revealing strong signal in the silver region and thus confirms the formation of silver nanoparticles

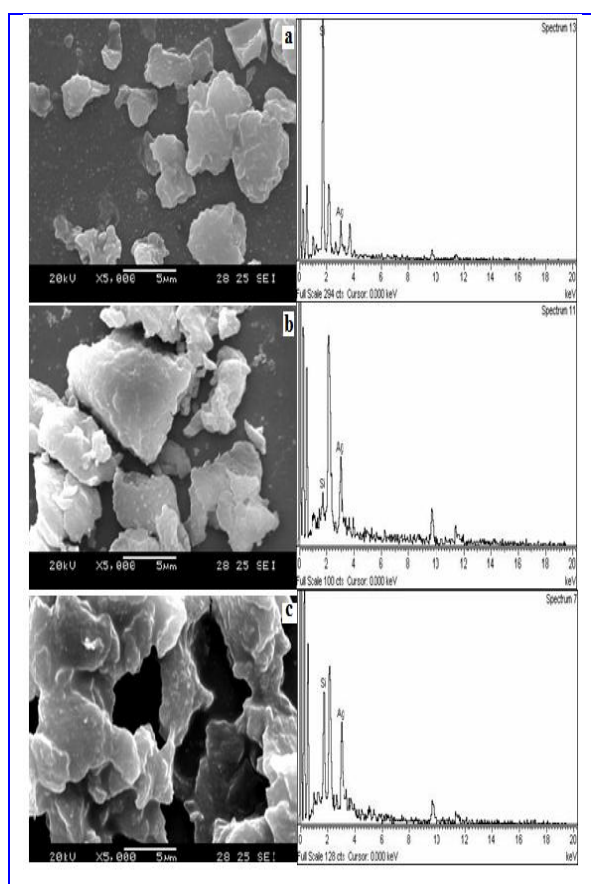


Fig. 4: SEM image with EDX spectrum of (a) 0.4, (b) 0.8 and (c) 1.2% w/v are different concentration of Ag/Dx Nanoparticles

3.5. Atomic Force Microscopy (AFM)

The 1.2 % w/v concentration of Dextran is found to be optimum for the synthesis of high concentration of AgNPs. The Ag/Dx nanoparticles prepared from 1.2 % w/v of Ag is chosen for AFM characterization. The particle size of Ag nanoparticles is a significant issue in killing microorganisms; surface topography was conducted on NPs obtained

from colloidal silver solutions by Atomic Force Microscopy in order to show morphological changes and to determine the size of the nanoparticles on the surface. Almost all of the silver nanoparticles determined as small particles were equally spread and uniformly distributed (Fig. 5). The size of particles was in the range ~20–52 nm. Smaller sized Ag nanoparticles have many positive attributes, such as good conductivity, chemical stability, and catalytic and antibacterial activity, which would make them suitable for many practical applications. The tapping mode AFM image clearly shows the formation of nanoparticles with spherical or steroidal shape. Owing to agglomeration of particle only approximate sizes are reported. The size of the particle is 52 nm.

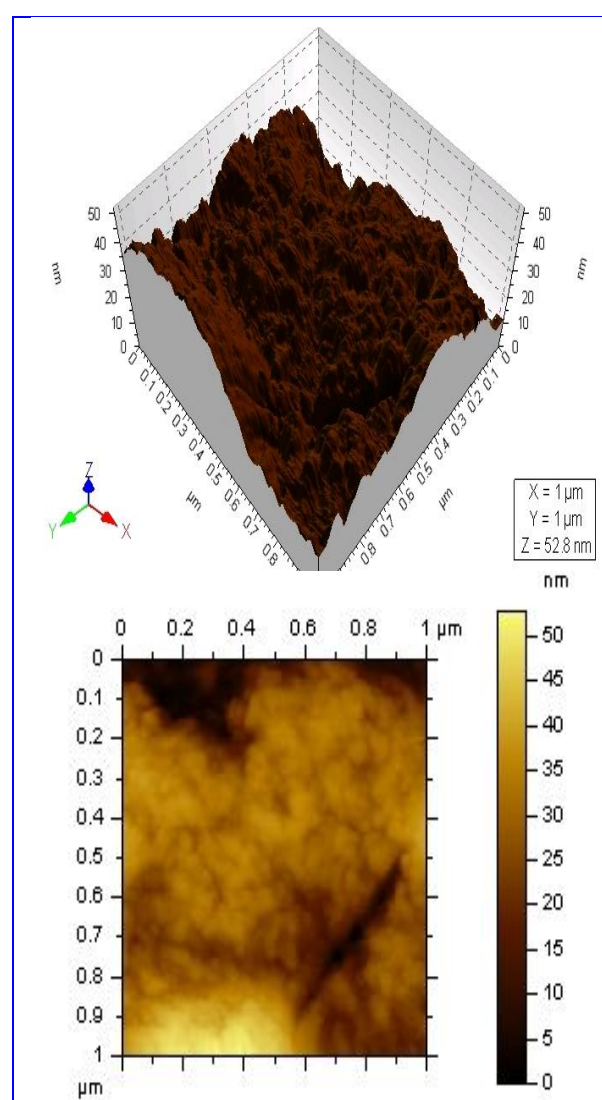


Fig. 5: Surface topography of 3-Dimensional image and height of Ag/Dx nanoparticle of 1.2% w/v at constant temperature (80 °C)

4. CONCLUSION

In conclusion, Ag nanoparticles have been prepared by chemical reduction of AgNO₃ using Dextran at 80°C. Dextran acts as a reducing and stabilizing agent for the synthesis of silver nanoparticles. The developed silver nanoparticles are well characterized using different techniques, to confirm the formation of silver nanoparticles. The developed silver nanoparticles are well characterized using different techniques, to conform the formation of silver nanoparticles. The morphology of nanocomposite was examined by SEM with and AFM. FT-IR, XRD and UV-Visible spectra reveled the formation of silver nanoparticles.

REFERENCES

- Pillai, Z. S. and Kamat, P. V., What Factors Control the Size and Shape of Silver Nanoparticles in the Citrate Ion Reduction Method, *J. Phys. Chem. B.*, 108(3), 945-951 (2004).
doi:10.1021/jp037018r
- Guenther, B., Kumpmann, V. and Kunze, H. D., Secondary recrystallization effects in nanostructured elemental metals, *Scr. Met. Mat.*, 27(7), 833-838 (1992).
doi:10.1016/0956-716X(92)90401-Y
- Li, J., Lin, Y. and Zhao, B., Spontaneous Agglomeration of Silver Nanoparticles Deposited on Carbon Film Surface, *J. Nanoparticle Res.*, 4(4), 345-348 (2002).
doi:10.1023/A:1021120723498
- Brust, M. and Kiely, C. J., Some recent advances in nanostructure preparation from gold and silver particles: a short topical review, *Coll. Surf. A: Phys.-Chem. Eng. Asp.*, 202(3), 175-186 (2002).
doi:10.1016/S0927-7757(01)01087-1
- Mulvaney, P., Wilson, O. and Wilson, G. I., Laser Writing in Polarized Silver Nanorod Films, *Adv. Mater.* 14(13), 1000-1004 (2002).
doi:10.1002/1521-4095(20020705)14:13/14<1000::AI D-ADMA1000>3.0.CO;2-E
- Tan, Y., Li, Y. and Zhu, D. J., Preparation of silver nanocrystals in the presence of aniline, *Colloid Interface Sci.* 25(2), 244- (2003).
doi:10.1016/S0021-9797(02)00151-0
- Yu, D. and Yam, V. W. W., Structural and Electrochemical Characterization of Nanocrystalline Li[Li_{0.12}Ni_{0.32}Mn_{0.56}]O₂ Synthesized by a Polymer-Pyrolysis Route, *J. Phys. Chem. B*, 109(3), 18772-18776 (2005).
doi:10.1021/jp0464369
- Xie, J., Lee, J. Y., Wang, D. I. C., and Ting, Y. P., Silver Nanoplates: From Biological to Biomimetic Synthesis, *ACS Nano*, 1(5), 429-439 (2007).
doi:10.1021/nn7000883
- Kim, M., Byun, J. W., Shin, D. S. and Lee, Y. S., Spontaneous formation of silver nanoparticles on polymeric supports, *Mat. Res. Bull.* 44(2), 334-338 (2009).
doi:10.1016/j.materresbull.2008.05.014
- Taleb, C., Petit, M. and Pileni, P., Synthesis of Highly Monodisperse Silver Nanoparticles from AOT Reverse Micelles: A Way to 2D and 3D Self-Organization, *Chem. Mater.*, 9(4), 950-959 (1997).
doi:10.1021/cm960513y
- Henglein, A., Reduction of Ag(CN)₂- on Silver and Platinum Colloidal Nanoparticles, *Langmuir*, 17(8), 2329-2333 (2001).
doi:10.1021/la001081f
- Esumi, K., Tano, T., Torigoe, K. and Meguro, K., Preparation and characterization of bimetallic palladium-copper colloids by thermal decomposition of their acetate compounds in organic solvents, *Chem. Mater.*, 2(5), 564-567 (1990).
doi:10.1021/cm00011a019
- Zhu, J. J., Liu, S. W., Palchik, O., Koltypin, Y. and Gedanken, A., hape Selectivity in Adsorption on the All-Silica DD3R, *Langmuir* 16(7), 3322-3329 (2000).
doi:10.1021/la9914007
- Sharma, V. K., Yngard, R. A. and Lin, Y., Silver nanoparticles: Green synthesis and their antimicrobial activities, *Ads. Colloid Interface Sci.* 145(2), 83-96 (2009).
doi:10.1016/j.cis.2008.09.002
- Al-Thabaiti, S. A., Al-Nawaiser, F. M., Obaid, A., Al-Youbi, A. O. and Khan, Z., Formation and characterization of surfactant stabilized silver nanoparticles: A kinetic study, *Colloids Surfs. B: Biointerfaces*, 67(2), 230-237 (2008).
doi:10.1016/j.colsurfb.2008.08.022
- Khan, Z., Al-Thabaiti, S. A., El-Mossalamy, E. H. and Obaid, A. Y., Studies on the kinetics of growth of silver nanoparticles in different surfactant solutions, *Colloids Surf B: Biointerfaces*, 73(2), 284-288 (2009).
doi:10.1016/j.colsurfb.2009.05.030
- Won, H. I. I., Nersisyan, H., Won, C. W., Lee, J. M. and Hwang, J. S., Preparation of porous silver particles using ammonium formate and its formation mechanism, *Chem Eng J.*, 156, 459-464 (2010).
- Rodríguez-Fernández, D., Pérez-Juste, J., Pastoriza Santos, I., Liz-Marzán, L. M., Colloidal Synthesis of Gold Semishells *ChemistryOpen*, 1(27), 90-95 (2012).
- Kim, D. S., Jung, Y. J. and Kim, Y. M., Synthesis and Properties of Dextran-Linked Ampicillin, *Drug*

- Development and Industrial Pharmacy 27(1), 97–101 (2001).
[doi:10.1081/DDC-100000133](https://doi.org/10.1081/DDC-100000133)
- Yura, H., Synthesis and pharmacokinetics of a novel macromolecular prodrug of Tacrolimus (FK506), FK506–dextran conjugate, Journal of Controlled Release 57(1), 87–99 (1999).
[doi:10.1016/S0168-3659\(98\)00150-3](https://doi.org/10.1016/S0168-3659(98)00150-3)
- Bat tersby, Synthesis and pharmacokinetics of a novel macromolecular prodrug of Tacrolimus (FK506), FK506–dextran conjugate, J., Journal of Controlled Release 42(1), 143–156 (1996).
- Solmon, D., Sally, Synthesis and Study of Silver Nanoparticles, Journal of Chemical Education, 84(2), 322–325 (2007).
[doi:10.1021/ed084p322](https://doi.org/10.1021/ed084p322)
- Mathlouthi, M. and Koenig, J. L., Advances in Carbohydrate Chemistry and Biochemistry, AdvCarbohydr Chem Biochem 44, 7-89 (1986).
[doi:10.1016/S0065-2318\(08\)60077-3](https://doi.org/10.1016/S0065-2318(08)60077-3)
- Abargues, R., Albert, S., Valdes, J. L., Abderrafi, K. and Martinez-Pastor, J. P., Molecular-mediated assembly of silver nanoparticles with controlled interparticle spacing and chain length, J. Mater. Chem. 22(41), 22204–22211 (2012).
[doi:10.1039/c2jm34707e](https://doi.org/10.1039/c2jm34707e)